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SEAL PRINT  
[Shiru Purinto]

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UNITED STATES PATENT AND TRADEMARK OFFICE  
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[Translator's note: Amendment is incorporated in the main text - although the insertion of amendment is rather confusing, the translator did the best he could.]

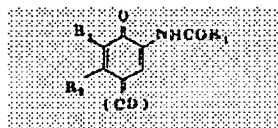
## 1. Title of Invention

Seal Print

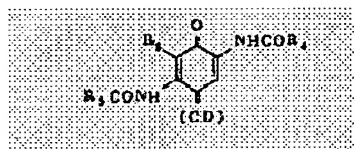
## 2. Claim

(1) A seal print on which are disposed a color photographic printing paper on which an image has been printed and an adhesive layer on the back surface of this, the invention characterized as follows; the abovementioned color photographic printing paper is made by disposing a yellow colored layer, a magenta colored layer and a cyan colored layer on a support; in addition, an image which is on said cyan colored layer is comprised of a cyan pigment indicated in general formula (1) or general formula (2) obtained by reacting an acid of an aromatic primary amine developing agent (hereinafter referred to as "CD") and a cyan coupler;

General formula (1)



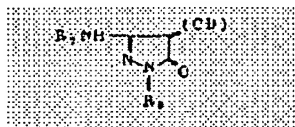
General formula (2)



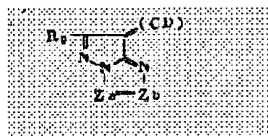
\* Numbers in the margin indicate pagination in the foreign text.

in addition, the image on the magenta colored layer is comprised of a magenta hue obtained by reacting the CD and the magenta colored coupler represented by general formula (3) or (4);

General formula (3)



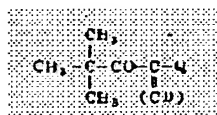
General formula (4)



in addition, the yellow colored layer is comprised of a yellow pigment obtained by reacting the CD and the coupler and represented by general formula (5);

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
General formula (5)



where R<sub>1</sub>, R<sub>4</sub> and R<sub>5</sub> are respectively an aliphatic group, an aromatic group or a heterocyclic amino group; R<sub>2</sub> is an aliphatic group, R<sub>3</sub> and R<sub>6</sub> are respectively a hydrogen atom, a halogen group, an aliphatic group, an aliphatic oxy group or an acyl amino group; R<sub>7</sub> and R<sub>8</sub> represent a non-substitutional or a substitutional phenyl group; R<sub>9</sub> is a hydrogen atom or a substitutional group;

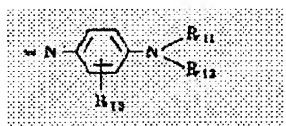
R<sub>2</sub> and R<sub>3</sub> as well as R<sub>5</sub> and R<sub>6</sub> respectively may combine to form a 5 to 7-member group;

Q is a substitutional or non-substitutional N-phenyl carbamoyl group; Z<sub>a</sub> and Z<sub>b</sub> represent a -CH= group

 -C= group or -N= group; R<sub>10</sub> represents a substitutional group; (CD) represents a coupling residue of an acid of an aromatic primary amine developing agent.

(2) A seal print as described in Claim 1 wherein the abovementioned (CD) is a residue which is represented by the following general formula (6);

General formula (6)



where R<sub>11</sub>, R<sub>12</sub> represent a substitutional or non-substitutional alkyl group; R<sub>3</sub> represents a hydrogen atom or a substitution group; the number of these substitutions may be an integer of 1 to 4.

(3) A seal print as described in Claim 1 wherein at least one of the abovementioned cyan, magenta and yellow colored layers is not water-soluble and contains an organic solvent-soluble polymer.

(4) A seal print as described in Claim 1 wherein the abovementioned color photographic printing paper is 50 to 200  $\mu$ m thick.

(5) A seal print as described in Claim 1 wherein the carrier of the abovementioned color photographic printing paper is a metal foil membrane layer the back surface of which has a mirror finish surface reflectivity or has a second type of dispersion reflectivity.

### 3. Detailed Description of Invention

(Industrial Field)

The present invention relates to a high quality seal print which is pleasant in appearance with a good finish. It relates particularly to a seal print which resists rough handling and which is resistant to high humidity and heat.

(Problems Which the Present Invention is Intended to Solve)

The so-called seal print in which an adhesive layer is disposed on the back surface of a color photographic printing paper, with a printed image, for which any size can be selected and which can be pasted freely to another mount is known on the basis of the Specification of Japanese Laid-Open Patent 60-41950 and the Specification of Japanese Laid-Open Patent 60-41949. This color photographic printing paper which is used for this seal print does not overlap even when pasted to another sheet nor is it unpleasant to the touch. As a result, it was made thinner and the whiteness of the printed declined. In addition, when the colored photographic printing paper on the seal print was pasted to a postcard, it was handled roughly just like regular postcards and was exposed to high humidity and heat. There was also a need for it to be approximately

50  $\mu$  to 200  $\mu$ m thick and to be light weight. As a result, colored photographic printing paper could not be used as is for regular photographic printing. When the carrier was made thinner to make the paper thinner, not only did the physical strength decline but the moisture permeability become stronger and the durability of the image declined. People were also uncomfortable when they felt the difference between the background whiteness between the photographic printing paper and the paper mount. As a result, there was a need to suitably reduce the background whiteness of the photographic printing paper. Therefore, there is a need for a combination of image configuration pigments with clearly defined colors on a level with or greater than the prior art in order to provide a commercially viable image with a so-called pleasant appearance on the carrier.

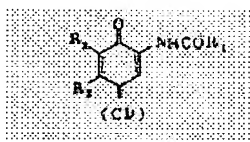
It is an object of the present invention to provide a seal print with a pleasant appearance using a photographic printing paper having a thickness of approximately 50  $\mu$  to 200  $\mu$  having a somewhat low whiteness; it is another object of the present /335 invention to provide a seal print having outstanding image durability relative to high humidity and heat. It is yet another object of the present invention to provide a seal print having a colored layer which is thin and which has good physical strength.

(Means Used to Solve the Problems)

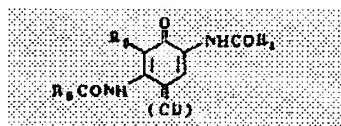
The objectives of the present invention have been attained as follows.

The abovementioned colored photographic printing paper is made by disposing a yellow colored layer, a magenta colored layer and a cyan colored layer on the carrier for the seal print which is made by disposing a colored photographic printing paper with a printed image on it and an adhesive layer which is disposed on the back of this. In addition, the image on said cyan colored layer is comprised of a cyan pigment represented in general formula (1) or general formula (2) and obtained by reacting an acid of an aromatic primary amine developer (hereinafter referred to as "CD") and a cyan coloring coupler.

General formula (1)

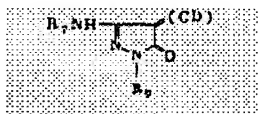


General formula (2)



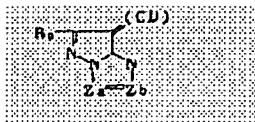
In addition, the image on the magenta colored layer is comprised of a magenta pigment represented in general formula (3) or general formula (4) by reacting the CD and the magenta colored coupler.

General formula (3)



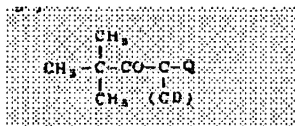
General formula (4)





The yellow colored layer is also comprised of a yellow pigment represented by general formula (5) and obtained by reacting the CD and the yellow colored coupler.

General formula (5)



Where  $R_1$ ,  $R_4$  and  $R_5$  are respectively an aliphatic group, an aromatic group or a heterocyclic amino group;  $R_2$  is an aliphatic group,  $R_3$  and  $R_6$  are respectively a hydrogen atom, a halogen group, an aliphatic group, an aliphatic oxy group or an acyl amino group.  $R_7$  and  $R_8$  represent a non-substitutional or a substitutional phenyl group.  $R_9$  is a hydrogen atom or a substitutional group.

$R_2$  and  $R_3$  as well as  $R_5$  and  $R_6$  respectively may combine to form a 5 to 7-member group.

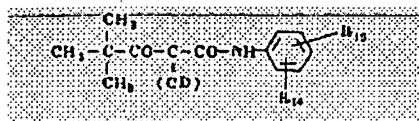
$Q$  is a substitutional or non-substitutional N-phenyl carbamoyl group.  $Za$  and  $Zb$  represent  $-CH =$  group



$-C =$  group or  $-N =$  group.  $R_{10}$  represents a substitutional group. (CD) represents a coupling residue of an acid of an aromatic primary amine developing agent.

Next, we shall describe the characteristics of the present invention. The first characteristic is the pigment which is formed on the colored layer. The pigment in the present invention is such that each photosensitive layer which most typically comprises halogenated silver grains and a color coupler with increased spectral sensitivity are subjected to color developing processing after exposure so that an acid of the paraphenylene diamine derivative, which is the main chemical constituent in the coloring and developing process, and said coupler is subjected to a coupling reaction. The yellow pigment is obtained by an oxidation coupling reaction with the acyl acetanilide type coupler and the paraphenylene diamine derivative. However, of these, a pigment obtained from a pivaroyl acetanilide type coupler /336 is preferable. This pigment is advantageous in that it is cut so that the long wave end of the spectral absorption is sharp and it has outstanding durability. It is dispersed in a hydrophilic colloid using small amounts of an organic solvent more easily than the benzoyl acetanilide main nucleus. It is also not water-soluble, it readily dissolves in an organic solvent soluble polymer and it provides a physically strong colored layer. The yellow pigment in the present invention should be a pigment represented by general formula (5-1).

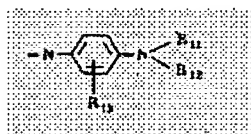
General formula (5-1)



Where R<sub>14</sub>, R<sub>15</sub> are a hydrogen atom (both cannot be hydrogen atoms) or a substitutional group usually used for yellow couplers, such as an alkyl group, an alkenyl group, an alkoxy group, an alkoxy carbonyl group, a halogen atom, an alkoxy carbamoyl group, an aliphatic amide group, an alkyl sulfamoyl group, an alkyl sulfone amide group, an alkyl ureide group, an alkyl substitution succinyl group, an aryl oxy group, an aryl oxy carbonyl group, an aryl carbamoyl group, an aryl amide group, an aryl sulfamoyl group, an aryl sulfone amide group, an aryl ureide group, a carboxy group, a sulfo group, a nitro group, a cyano group, a thiocyano group and others. The substitutional group of these may be the same or different. The coupler may be a polymer coupler equivalent to greater than a bis-body.

(CD) should be the coupling residue of a phenylene diamine derivative represented by the following general formula (6).

General formula (6)

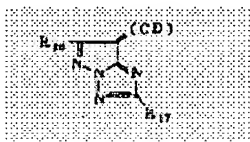


where R<sub>11</sub>, R<sub>12</sub> are respectively a substitutional or non-substitutional alkyl group. The alkyl group should have 1 to 4 carbon atoms.

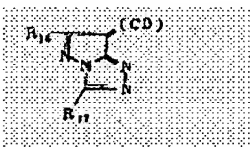
Specific examples of this substitutional group are a hydroxy group, an alkyl sulfone amide group, an alkoxy group and the like. Specific examples of  $R_{11}$  and  $R_{12}$  are an ethyl group, a  $\beta$ -hydroxy ethyl group, a  $\beta$ -methane sulfone amide ethyl group, a  $\beta$ -methoxy ethyl group and the like.  $R_{13}$  represents a hydrogen atom or 1 to 4 substitution groups. An example of this substitution group is an alkyl group (for example, a methyl group and the like).

The magenta pigment in the present invention should be a pigment represented by the following general formulas (4-1) and (4-2).

General formula (4-1)



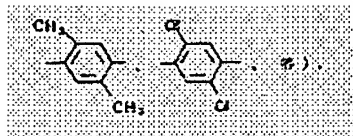
General formula (4-2)



Where  $R_{16}$  and  $R_{17}$  may be the same or different and indicate the following: a hydrogen atom, a halogen atom, an alkyl group, an aryl group, a heterocyclic group, a cyano group, an alkoxy group, an aryl oxy group, a heterocyclic oxy group, an acyl oxy group, a carbamoyl oxy group, a silyl oxy group, a sulfonyl oxy group, an acyl amino group, an anilino group, an ureide group, an imide group, a sulfamoyl

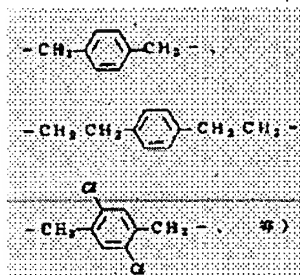
amino group, a carbamoyl amino group, an alkyl thio group, an aryl thio group, a heterocyclic thio group, an alkoxy carbonyl amino group, an aryl oxy carbonyl amino group,, a sulfone amide group, /337 a carbamoyl group, an acyl group, a sulfamoyl group, a sulfonyl group,, a sulfinyl group, an alkoxy carbonyl group and an aryl oxy carbonyl group. The following are especially suitable: an alkyl group, an alkoxy group, an alkyl thio group, an aryl group, an aryl oxy group, an aryl thio group, an acyl amino group and an anilino group.  $R_{16}$  or  $R_{17}$  may be a bivalent combination group and may form a bis-body. The residue of the pigment represented by general formulas (4-1) and (4-2) may be a polymer coupler present on the main chain or the side chain of the polymer and particularly should be a polymer derived from a vinyl monomer having a part which is represented by the general formula. In this case,  $R_{16}$ ,  $R_{17}$  represent a combination group which bonds with a vinyl group.

When the structure represented by general formulas (4-1), (4-2) is contained in the vinyl monomer, the combination group represented by  $R_{16}$ ,  $R_{17}$  includes groups which come about through combinations of an alkylene group (an alkylene group of a substitutional or non-substitutional group such as a methylene group, an ethylene group, a 1,10-decylene group,  $-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-$ , and the like), a phenylene group (a substitutional or non-substitutional phenylene group such as a 1,4-phenylene group, a 1,3-phenylene group,



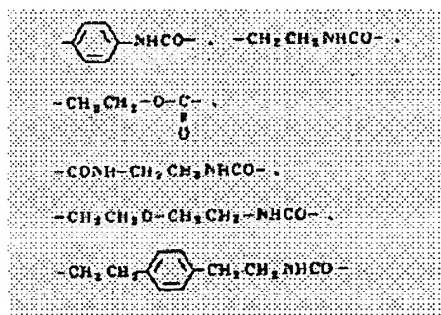
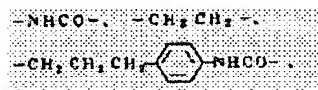
and the like),

-NHCO-, -CONH-, -O-, -OCO- and an aralkylene group (for example,



and the like).

Suitable combination groups are as follows.



Furthermore, this vinyl group may be substituted by another substitutional group in addition to the residue represented by general formula (4-1) or general formula (4-2). Suitable substitution groups are a chlorine atom or a lower alkyl group with 1 to 4 carbon

atoms (for example, a methyl group, an ethyl group, a butyl group and the like).

The polymer which has been derived from a vinyl monomer having a pigment may be a copolymerization polymer of an ethylene-like monomer with no coloring characteristics. Examples of this ethylene-like monomer with no coloring characteristics are: acrylic acid,  $\alpha$ -chloracrylic acid,  $\alpha$ -aracrylic acid (for example, methacrylic acid and the like) and esters or amides which are derivatives of these acrylic acids (for example, acryl amide, n-butyl acrylic amide, t-butyl acrylic amide, iso-butyl acrylate, 2-ethyl hexyl acrylate, n-octyl acrylate vinyl propionate and vinyl laurate), acrylonitrile, methacrylonitrile, aromatic vinyl compounds (for example, styrene and derivatives thereof, vinyl toluene, divinyl benzene, vinyl acetophenone and sulfostyrene), itaconic acid, citraconic acid, crotonic acid, vinylidene chloride, vinyl alkyl ether (for example, vinyl ethyl ether), maleic acid, anhydrous maleic acid, ester maleate, N-vinyl-2-pyrrolidine, N-vinyl pyridine as well as /338 2- or 4-vinyl pyridine and the like. Acrylic esters, methacrylic esters and maleic esters are especially suitable. Two or more types of these ethylene-like unsaturated monomers with no coloring characteristics may be used together.

Examples of these are: n-butyl acrylate and methyl acrylate, styrene and methacrylate, methyl acrylate and diacetone acryl amide and the like.

As is well known in the polymer color coupler field, ethylene-like unsaturated monomers with no coloring characteristics used for copolymerization with solid water-insoluble monomer couplers may be selected for their positive effect on physical characteristics and/or chemical characteristics such as solubility, compatibility with the bonding agent of the photographic colloid composition such as gelatin, flexibility, heat stability and the like.

The characteristics of the magenta pigment in the present invention include small amounts of second absorption or none at all on the short wave side include the spectral absorption characteristics wherein the absorption of the long wave side is cut sharp; and its outstanding durability vis-à-vis high humidity and heat. In addition, when the magenta pigment is a polymer, it is dispersed as latex so that a high-boiling point organic solvent need not be used or the amount used can be reduced. As a result, the coating on the colored layer can be made thin and the physical strength can be upgraded.

The cyan pigment in the present invention is obtained through the oxidation coupling reaction of the coupler and the paraphenylene diacy group coloring and developing main chemical constituent. This paraphenylene group cyan coupler may be used in combination with a naphthol group cyan coupler. The naphthol group cyan coupler may be the naphthol group coupler described in United States Patent 2,474,293 and preferably that described in US Patent 4,052,212, US



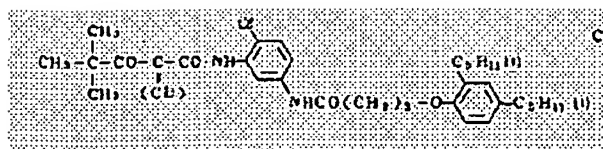
Patent 4,146,396, US Patent 4,228,233 and US Patent 4,296,200. The phenol group coupler may be that described in United States Patent 2,369,929, US Patent 2,801,171, US Patent 2,772,162, US Patent 2,895,826 and the like. A typical example of the cyan coupler which is resistant to humidity and temperature to be used in the present invention is the phenol group cyan coupler having an alkyl group at or beyond an ethyl group on the meta position of the phenol nucleus described in United States Patent 3,772,002 and described in United States Patent 2,772,162, US Patent 3,758,308, US Patent 4,126,396, US Patent 4,334,011, US Patent 4,327,173, West German Patent 3,329,729 and European Patent 121,365 and the like; or the coupler described in United States Patent 3,446,622, US Patent 4,333,999; US Patent 4,451,559 and US Patent 4,427,767 and the like.

The cyan pigment in the present invention is used to cover a wavelength region of 600 to 700 m $\mu$  by combining two or more pigments represented by general formula (1) or (2). It is advantageous in that it can obtain a pigment image with little absorption on the short-wave side and it has outstanding durability vis-à-vis high humidity and heat.

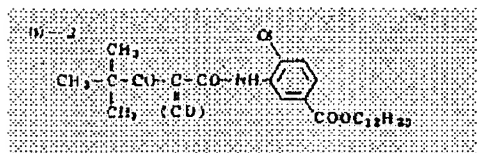
Next, we shall provide specific examples of the pigment in the present invention. However, it should by no means be construed that the present invention is restricted to these practical examples.

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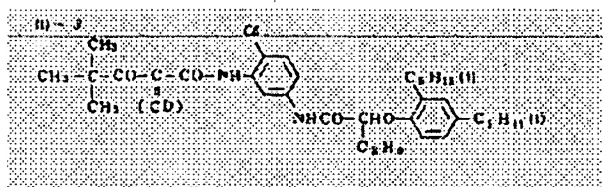
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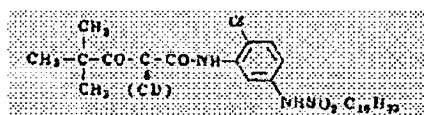
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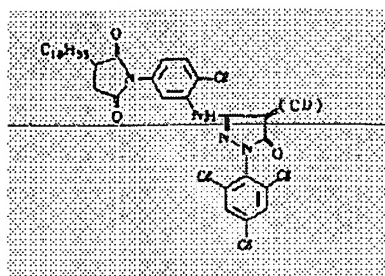
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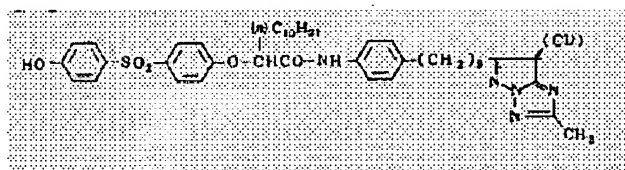
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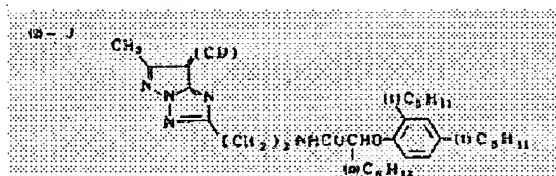
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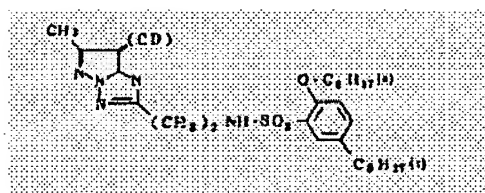
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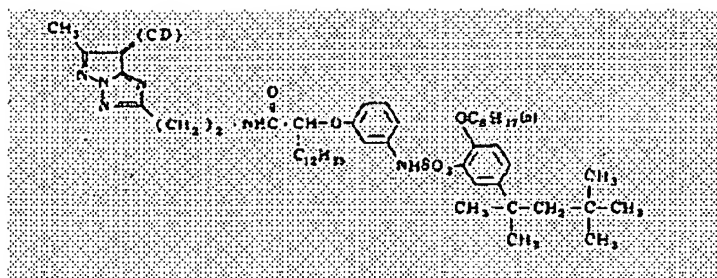


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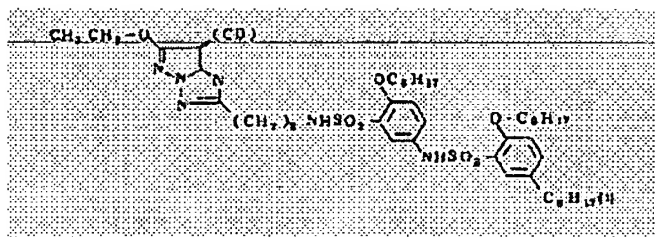


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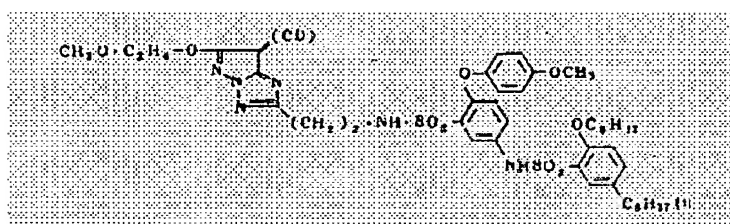
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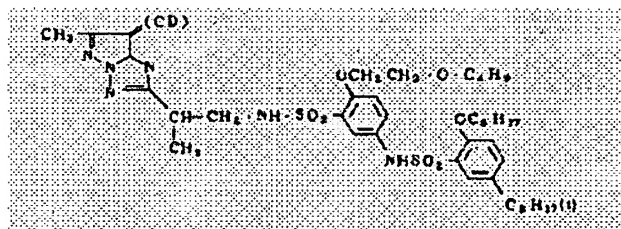
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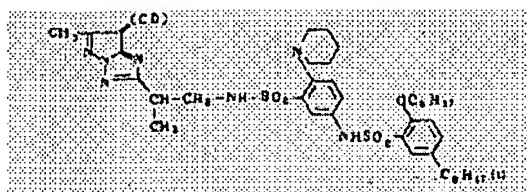


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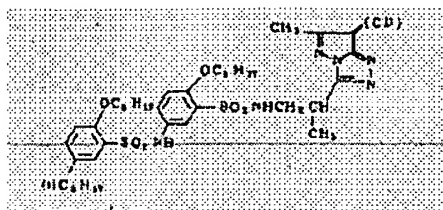


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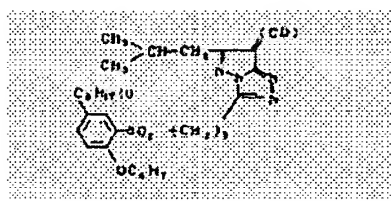
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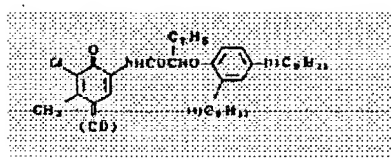
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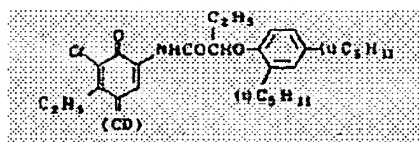
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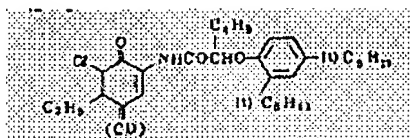
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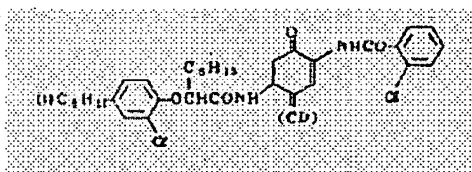
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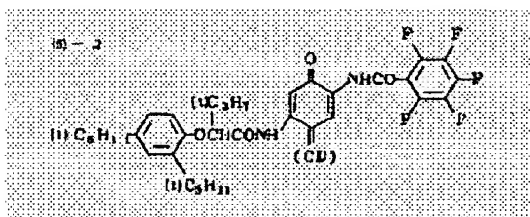
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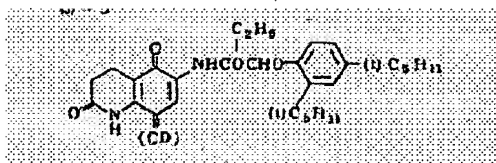
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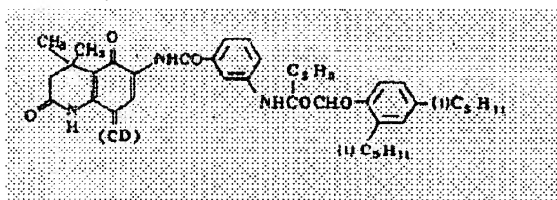
(5) - 2

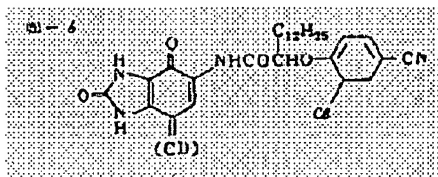
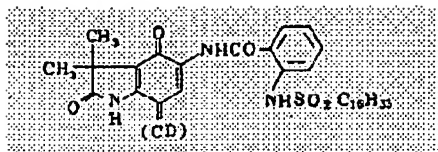


(5) - 3

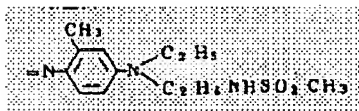


(5) - 4

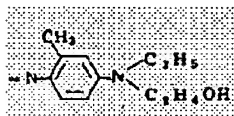




The specific example (CD) represents in its entirety



The other (CD) may be a coupling residue for



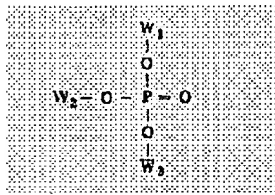
and other p-phenylene diamine derivatives.

The pigment which forms the image in the present invention should be a combination of one, two or more coexistent combinations of high-melting point organic solvents represented by following general formulas (7), (8), (9), (10) and (11). Details of these are

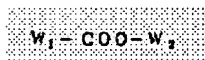
described on pages 440 to 470 of Japanese Patent Application 61-32462. A coexisting polymer which is water-insoluble and organic solvent-soluble as described in Japanese Patent Publication 48-30474, United States Patent 3,619,195 and Japanese Patent Application 61-162813 and others is especially suitable.

Comment[AS1]: last sentence missing.

General formula (7)



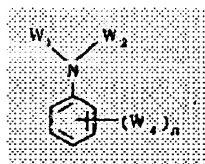
General formula (8)



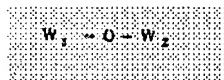
General formula (9)



General formula (10)



General formula (11)





(where  $W_1$ ,  $W_2$  and  $W_3$  are respectively a substitutional or non-substitutional alkyl group, cycloalkyl group, alkenyl group, aryl group or heterocyclic group;  $W_4$  represents  $W_1$ ,  $OW_1$  or  $S - W_1$ ;  $n$  is an integer of 1 through 5; when  $n$  is 2 or more,  $W_4$  may be the same or different. In general formula (11),  $W_1$  and  $W_2$  may form a condensed ring).

Next we shall provide specific examples of a suitable organic solvent-soluble polymer. However, it should by no means be construed that the present invention is restricted to these.

(P -1) polyvinyl acetate

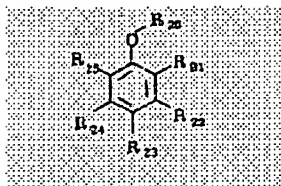
(P -2) polyvinyl propionate

(P -3) polymethyl methacrylate

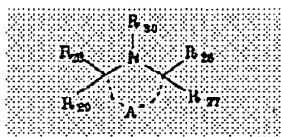
In addition, the specific examples (P -4) to (P -69) of the polymer described on pages 32 to 39 of the Specification of Japanese Laid-Open Patent Application 61-162813 and the specific examples 1 through 35 of the polymer described in Japanese Laid-Open Patent Specification 48-30494 may also be used.

These polymers may be combined with the abovementioned high-boiling point organic solvent.

In addition, the pigment in the present invention should also contain a color fading prevention agent or an oxidation inhibitor represented by the following general formulas (12) or (13). Of these, an organic solvent-soluble compound is particularly suitable.



General formula (13)



Where  $R_{20}$  is a hydrogen atom, an aliphatic group, an aromatic group, a hetero ring or a hydrolysable protective group.  $R_{21}$ ,  $R_{22}$ ,  $R_{23}$ ,  $R_{24}$  and  $R_{25}$  may be the same or different and represent a hydrogen atom or a substitutional group.  $R_{30}$  represents a hydrogen atom, an aliphatic group, an acyl group, a sulfonyl group, a sulfinyl group, an oxy radical group or a hydroxy group. A represents a non-ferrous metal atom group required to form a five-member, six-member or seven-member ring.

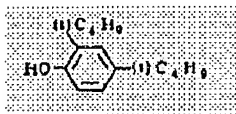
$R_{26}$ ,  $R_{27}$ ,  $R_{28}$  and  $R_{29}$  may be the same or different and they represent respectively a hydrogen atom or an alkyl group.

Of the substitutional groups represented in general formula (12),  $R_{20}$  and  $R_{21}$  or  $R_{22}$ ,  $R_{23}$ ,  $R_{24}$ ,  $R_{25}$  and  $R_{26}$ , those at an ortho position may combine with one another and form five-member, six-member or seven-member rings.

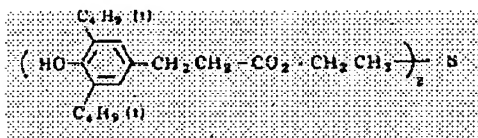
Of the substitution groups represented by general formula (13),  $R_{26}$  and  $R_{27}$ ,  $R_{28}$  and  $R_{29}$  or  $R_{30}$  and  $R_{26}$  may combine with one another and form five-member, six-member or seven-member rings.

Next, we shall provide specific examples of the compounds represented by general formulas (12), (13), however, it should by no means be construed that the present invention is restricted to these.

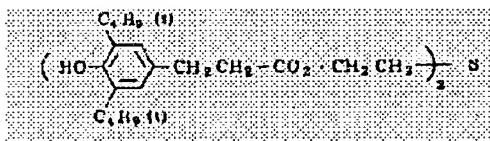
(12) 1



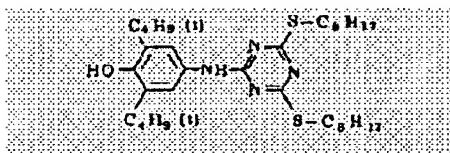
(12) - 2



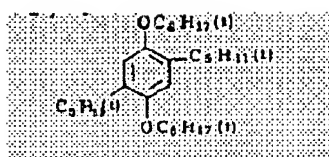
(12) - 3



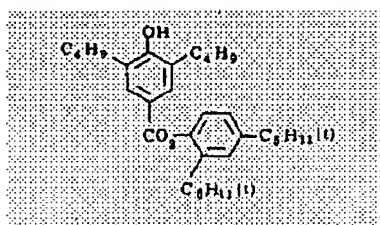
(12) - 4



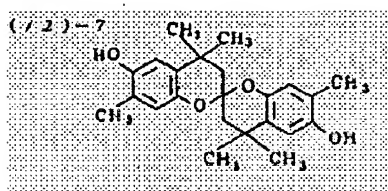
(12) - 5



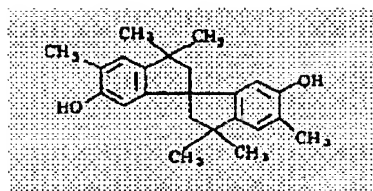
(12) - 6



(12) - 7

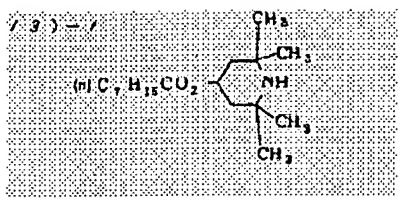


(12) - 8

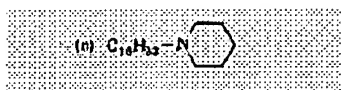




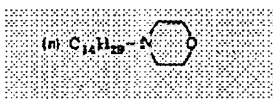
(13) - 1



(13) - 2



(13) - 3



In a suitable mode for the seal print in the present invention, a yellow colored layer containing a blue-sensitive halogenated silver emulsion and a yellow colored coupler, a magenta colored layer containing a green-sensitive halogenated silver emulsion and a magenta colored coupler and a cyan colored layer containing a red-sensitive halogenated silver emulsion and a cyan coupler are exposed like an image on a color photographic printing sheet on which a yellow filter layer, a protective layer and the like are disposed. Then, coloring and developing are carried out and the color print is formed. An adhesive layer is also disposed on the back surface of this and it can be made into a commercial product by pasting onto a backing.

A mold release paper or an official postcard may also be used as a backing.

A resoluble paste and hot melting type of adhesive, microcapsule-type of pressurized adhesive and the so-called tacky adhesive are used for the adhesive used in the present invention. When a tacky adhesive layer is disposed, a mold release paper or sheet may be disposed. The tacky adhesive used in the present invention is a raw material which adheres to and comes off rapidly when pressurized to another mount and with heat, light, solvent, chemical reactions and other means when stuck beforehand to the carrier to form a layer shape. The basic constituent of the tacky adhesive is a polymer substance thereby providing a strong cohesive force and elasticity. Synthetic polymers and elastomers are /345 oftentimes used for this. Polymer substances which provide adhesiveness and the so-called adhesive providing agents are also used. In addition, the adhesiveness and cohesive force are regulated, the surface adhesiveness between the back surface of the carrier and the adhesive is enhanced and thin layers can be readily formed so that a softener and bulking agent are used. In addition, an anti-oxidant, UV absorption agent, oxygen intercepting agent and the like are used to stabilize the image, discolor and stabilize the adhesive agent layer and to prevent mold and the like.

The following are examples of the raw material which may be used.

The following synthetic polymers and elastomers may be used: polyacrylate, acryl copolymers, vinyl chloride-vinyl acetate copolymers, polyvinyl butyral, polyvinyl isobutyral ether, polyvinyl alcohols, natural rubber, butyl rubber, polyisoprene rubber, recycled rubber, chloroprene, polyisobutylene, silicone rubber, chloride rubber, chlorinated rubber and the like.

The following adhesiveness providing agents may be used: rosin, ester gum, polyolefin group petroleum resins, polyterpene group polymers, cumarone, indene group polymers, styrene group polymers, phenol resins, xylene group polymers, gum arabic, dextrin and glue and the like.

The following may be used as the softener: plasticizers of the abovementioned polymer substances, polybutene, polyisobutylene low grade polymers, polyvinyl isobutyl ether low grade polymers, rosin oil, rubber depolymers, lanoline, wax, vegetable oils and the like.

The following may be used as the packing agent: titanium chloride, silica, alumina, barium sulfate, starch, clay, polymer fine grain latex and the like.

The following may be used as the oxidation inhibitor: hydroquinones (2,5- di (t) butyl hydroquinone and the like), phenols (2,6- di (t) butyl-4-methyl phenol, 1,1-bis (4-hydroxy phenol), cyclohexane, p-alkoxy phenols, cyclohexane, p-alkoxy phenols, bisphenols, hindered phenols, aminophenols and the like), curomanes (6-hydroxy curomanes, 5-hydroxy curomanes, spirocuromanes and the



like), gallic acid derivatives, aminophenols, hindered amines and the like.

The following may be used as stabilizers and fungicides:

benzothiazoline, isothiazolone, 4-thiazoline, benzimidazole, halogenated phenol, sulfanyl amide, benzotriazole and the like.

Mixtures of these may be disposed for the adhesive agent layer: 0.1 g to 30 g and preferably approximately 0.5 g to 20 g per  $\text{m}^2$ . The method of disposing these depends on the purpose and regular adhesive tape, adhesive sheet, label paper, free album and other methods may be used. Examples of these methods are described in Japanese Laid-Open Utility Model 60-41950, the Specification of Japanese Laid-Open Patent 61-23673, the Specification of Japanese Laid-Open Patent 61-60771, the Specification of Japanese Laid-Open Patent 61-83276, the Specification of Japanese Laid-Open Patent 61-103975, the Specification of Japanese Laid-Open Patent 61-148279, the Specification of Japanese Laid-Open Patent 61-148282, the Specification of Japanese Laid-Open Patent 61-174283 and the like.

The following may be used as the mold release paper or sheet used in the present invention: silicon-processed paper, Teflon-processed paper and the like, cellophane, film such as polyethylene, polypropylene, vinyl chloride, cellulose triacetate, polyethylene phthalate and synthetic paper or aluminum foil and the like. A mold release paper or sheet is used which can be readily made so that the adhesive force relative to the adhesive layer is weaker than the

adhesive force relative to the adhesive agent. For example, a thin layer (approximately 20  $\mu$  to 150  $\mu$  thick) of polyacrylene laminated paper, polyethylene terephthalate, aluminum foil and the like are suitable).

The halogenated silver emulsion used in the present invention may usually be produced by mixing a water-soluble silver salt (such as silver nitrate) solution and a water-soluble halogen salt (such as potassium bromide, sodium chloride and potassium iodide either singly or as mixtures of these) solution in the presence of a water-soluble polymer solution such as gelatin. Typical examples of the halogenated silver produced in this way are silver chloride, silver bromide as well as mixed halogenated silvers such as salt silver bromide, salt silver iodide bromide, iodine silver bromide and the like.

Halogenated silvers which should be used in the present invention may contain or may not contain silver iodide and should be salt iodine silver bromide with 3 % mol and under, iodine silver chloride or iodine silver bromide. The halogenated silver grains may be such that the inside and outer layer have different phases, they may have a multi-phase structure with a conjugate structure or the grains overall may be comprised of a uniform phase. They may also be mixed together. For example, the salt silver bromide grains having different phases may be nuclei which are richer in silver bromide than the average halogen composition or grains having a single layer or multiple layers inside the grain. These may also be nuclei which

are richer in silver chloride than the average halogen composition or may have a single layer or multiple layers inside the grain. As a result, the grain surface layer may be covered with a layer which is richer in silver bromide than the average halogen composition or conversely with a layer which is richer in silver chloride. The average grain size of the halogenated silver grains (when these are grains which are spherical or nearly spherical, the grain size is expressed in terms of grain diameter; when these are cubic grains, the grain size is expressed in terms of the length of the edge, which are respectively the average based on the projected area) should be not more than  $2\ \mu$  and not less than  $0.1\ \mu$  and particularly not more than  $1\ \mu$  and not less than  $0.15\ \mu$ . The distribution of the size may be either narrow or wide.

The so-called single dispersion halogenated silver emulsion having a narrow grain size distribution such that at least 90 % and particularly at least 95 % of all the grains is within  $\pm 40\%$  of the average grain size in terms of number or grains or in terms of weight may be used.

In addition, in order to satisfy the gradation which is the object of the goal for the photosensitive material, two or more types of simple dispersion halogenated silver emulsions having different grain sizes in the emulsion layer with essentially the same color sensitivity can be mixed in the same layer or a heavy layer may be coated on separately. In addition, a polydispersion halogenated

silver emulsion made of two or more types or a combination of a simple dispersion silver emulsion and a polydispersion silver emulsion may be mixed together or used by overlapping them.

The shape of the halogenated silver grains used in the present invention may be an octahedron, dodecahedron or decahedron type regular crystal or it may be irregular such as a spherical shape or complex shapes of these crystals may be used. Plate-shaped grains may be used and plate-shaped grains whose length/thickness ratio is a value of 5 or more and particularly 8 or more may use an emulsion which accounts for at least 50 % of the entire projected area of the grain. They may also be an emulsion comprised of a mixture of these types of crystal shapes. These types of emulsion may be the surface latent image type which forms mainly a latent image on the surface and may be an internal latent image type which is formed inside the grain.

The photographic emulsion used in the present invention can be produced using the method described in "Chimie et Physique Photographique" (Physical and Photographic Chemistry), by P. Glaflkides, Paul Montel Publishers, 1967; "Photographic Emulsion Chemistry", by G.F. Duffin, Focal Press, 1966; "Making and Coating Photographic Emulsion", by V.L. Zelikman et al., Focal Press, 1964). This means that the acidic method, the neutral method, the ammonia method and other methods may be used and the single-side mixing method, simultaneous mixing method and combinations of these may be

used as a means of reacting soluble halogen salt. The method (the so-called reverse mixing method) which involves forming grains in excess silver ions may also be used. One type of the simultaneous mixing method involves maintaining constant the  $pAg$  in the liquid phase which generates the halogenated silver, that is, the so-called "controlled double jet method". When this method is used, a halogenated silver emulsion having a regular crystal shape and a nearly uniform grain size can be obtained. In the process of shaping or physically maturing the halogenated silver grains, cadmium salt, zinc salt, lead salt, thallium salt, iridium salt or a complex salt thereof, rhodium salt or a complex salt thereof, iron salt or an iron complex salt thereof may coexist.

The halogenated silver emulsion is used for coating following the usual physical maturing after the grains have been formed, after desalting and after chemical maturing have been carried out.

When physical maturing is carried out in the presence of a halogenated silver emulsion (for example, ammonia, rhodan potassium or the thioether or thion compound described in United States Patent 3,271,157, Specification of Laid-Open Japanese Patent 51-12360, Specification of Laid-Open Japanese Patent 53-82408, Specification of Laid-Open Japanese Patent 53-144319, Specification of Laid-Open Japanese Patent 54-100717 or Specification of Laid-Open Japanese Patent 54-155828), a simple dispersion emulsion can be obtained which has a regular shape and a grain size distribution which is nearly

uniform. Nudel washing, the flocculation sedimentation method or the ultra-filtration method and the like may be used to remove soluble silver salt from the emulsion before and after physical maturing.

The halogenated emulsion used in the present invention may be chemically sensitized by combined use of sulfur or selen sensitization, reduction sensitization, precious metal /346 sensitization and other chemical sensitization independently or in combination.

This means that the sulfur sensitization method using a compound containing sulfur which can react with active gelatin and silver (for example, thiosulfate, thiourea, mercapto compounds, rodanines); the reduction sensitization method which uses a reduction substance (such as stannous salt, an amine, a hydrazine derivative, formamidine sulfinic acid, a silane compound); the precious metal sensitization method which uses metal compounds (such as metal complex salts, Pt, Ir, Pd, Rh, Fe and other Periodic Table Group VIII metal complex salts) may be used independently or in combination.

The photographic emulsion used in the present invention may be subjected to spectral sensitization using a photographic sensitization pigment.

A variety of compounds may be contained in the photographic emulsion used in the present invention to prevent bronzing while the photosensitive material is being manufactured, while it is being stored or during the photographic process and to stabilize the

photographic performance. This means that azoles such as a benzothiazolium salt, a benzimidazolium salt, an imidazole, a benzimidazole (preferably 5-nitrobenzimidazole), nitroindazole, benzotriazole (preferably 5-methyl benzotriazole), a triazole and the like; a mercapto compound such as a mercaptothiazole, a mercapto benzothiazole, mercaptobenzimidazole, mercaptobenzoxazole, mercaptooxy diazole, mercapto thiadiazole, mercapto triazole, mercapto tetrazole (particularly, 1-phenyl-5-mercapto tetrazole), a mercaptopyridine, a mercapto triadine and the like; for example, thiocarbonyl compounds such as oxazoline thion; an azaindene such as triazindene, tetrazaindene (particularly, 4-hydroxy-6-methyl-(1,3,3a, 7) tetrazaindene), pentazaindene and the like; benzene thiosulfonates, benzene sulfinates; benzenesulfonate amides; for example, adenine and other purines; and many other compounds may be added as a bronzing prevention agent or stabilizer.

The color photographic printing paper in the present invention may include an ultraviolet absorption agent in the protective layer, the intermediate layer or the colored layer. Examples are the benzotriazoles substituted by an aryl group described in United States Patent 3,553,794, US Patent 4,236,013, Specification of Laid-Open Japanese Patent 51-6540 and European Patent 57,160 and the like; the butadienes described in United States Patent 4,450,229 and US Patent 4,195,999; the cinnamic acid esters described in United States Patent 3,705,805 and US Patent 3,707,375; the benzophenones described

in United States Patent 3,215,530 and United Kingdom Patent 1,321,355; the polymer compounds having an ultraviolet absorption residue such as that described in United States Patent 3,761,272 and US Patent 4,431,726. An ultraviolet absorptive fluorescent whitener as described in United States Patent 3,499,762 and US Patent 3,700,455 may be used. A typical ultraviolet absorption agent is described in RD24239 (June 1984) and the like.

In addition, dyestuffs may be used as a filter, to prevent irradiation, to prevent halation and a variety of other purposes. This kind of dyestuff may be an oxonol dyestuff, a hemioxonol dyestuff, a styryl dyestuff, a merocyan dyestuff, an anthracene dyestuff, an azo dyestuff and the like. Besides these, a cyanine dyestuff, azomethine dyestuff, a triaryl methane dyestuff and a phthalocyanine dyestuff are also useful. An oil-soluble dyestuff may be emulsified using the water oil drop dispersion method and added to a hydrophilic colloid layer.

An inorganic or organic hardening agent is used to harden the multi-layer hydrophilic colloid layer which has been coated onto the carrier on the color photographic printing paper in the present invention. Examples of these are activated halogen compounds (2,4-dichloro-6-hydroxy-1,3,5-triazine and the like) and activated vinyl compounds (1,3-bis vinyl sulfonyl-2-propanol, 1,2-bis vinyl sulfonyl acetamide ethane or a vinyl group polymer and the like having a /347



vinyl sulfonyl group on its side chain) are suitable as they quickly harden the gelatin and other hydrophilic colloids and provide stable photographic characteristics. N-carbamoyl pyridinium salts and haloamidium salts are also outstanding because of their hardening speed.

The seal print or color photographic printing paper in the present invention should be flexible. Useful flexible backing materials or carriers are as follows: a film, web layer or  $\alpha$ -olefin polymer (for example, polyethylene polypropylene, ethylene/butene copolymers) comprised of semi-synthetic or synthetic polymers of cellulose nitrate, cellulose acetate, cellulose acetate butyrate, polystyrene, polyvinyl chloride, polyethylene terephthalate, polycarbonate and the like which are coated or laminated on paper and metal foil and the like. The carrier may be colored using a dyestuff and pigment. It may be black in order to intercept the light. The surfaces of these carriers are generally subjected to undercoating to improve the adhesiveness with the photographic emulsion layer and the like. Glow discharge, corona discharge, ultraviolet irradiation, flame processing and the like are carried out either before or after the surface of the carrier has been given an undercoating.

The carrier used in the present invention uses the abovementioned flexible carrier as a matrix, a metal foil coated layer having a mirror finish reflective surface or a second type of dispersed reflective surface is disposed on top of the carrier and

disposing an undercoating layer on top of this is particularly useful. The carriers described in Japanese Patent Application 61-52788, Japanese Patent Application 61-16880 and Japanese Patent Application 61-168801 are particularly suitable. The carrier should be approximately from 50  $\mu\text{m}$  to 190  $\mu\text{m}$  thick and preferably approximately from 50  $\mu\text{m}$  to 170  $\mu\text{m}$  thick. When this carrier is used, it has outstanding hue and image sharpness. As the metal foil coating is not penetrable by water, it particularly has outstanding durability vis-à-vis high humidity and heat.

The coloring and developing solution used for developing to make a marketable print for the sheet print in the present invention should be an alkaline aqueous solution having as its main constituent an aromatic primary amine group coloring and developing chemical. An amino phenol group compound is also useful as this coloring and developing main chemical constituent, however, a p-phenylene diamine group compound is preferable and 3-methyl-4-amino-N, N-diethyl aniline, 3-methyl-4-amino-N-ethyl-N- $\beta$ -hydroxyl ethyl aniline, 3-methyl-4-amino-N-ethyl-N-  $\beta$ -methane sulfone amide ethyl aniline, 3-methyl-4-amino-N-ethyl-N-  $\beta$ -methoxy ethyl aniline and sulfates and hydrochlorides thereof or p-toluene sulfonates and the like. These diamines are generally more stable as salts than in their free state.

The coloring and developing solution generally contains alkaline metal carbonates and borates or pH buffers such as phosphate, bromides, iodides, benzimidazoles, benzothiazoles or developing

inhibition agents or bronzing prevention agents such as mercapto compounds. In addition, hydroxy amines and derivatives thereof (for example, N,N-dialkyl substitutes) or preservatives such as sulfites, triethanol amines and derivatives thereof, organic solvents, such as diethylene glycol, benzyl alcohols, polyethylene glycol, quaternary ammonium salt, developing promotion agents such as amines, competitive couplers, nucleus creating agents such as sodium boron hydrides, auxiliary developing agents such as 1-phenyl-3-pyrazolidone, adhesive agents, a variety of chelating agents represented by amino polycarbonates, amino polyphosphonates, alkyl phosphonates and phospho/carbonates and the anti-oxidants described in West German Patent Application (OLS) 2,622,950 may be added to the coloring and developing solution.

When reverse color photographic printing paper is used in developing, coloring and developing are usually carried out after black and white developing has been carried out.

After coloring and developing have been carried out, the photographic emulsion layer is usually bleached. Bleaching may be carried out at the same time as the fixing or it may be carried out separately. In addition, a processing method which carries out bleaching and fixing after bleaching may be used to speed up the processing. Ethylene diamine tetraacetate iron (III) salt, diethylene triamine pentaacetate iron (II) salt and persulfite are suitable as a bleaching agent given their speedy processing and out of concern for

environmental pollution. In addition, an ethylene diamine tetraacetate iron (II) complex salt is particularly useful even in a separate bleaching solution and in a one-bath bleaching and fixing solution. Thiosulfite is generally used as a fixing agent. /348

Sulfite salt, hydrogensulfite or a carbonyl hydrogensulfite additive are suitable as a preservative for the bleaching and developing solution and for the fixing solution.

After bleaching and fixing or fixing has been carried out, washing and / or stabilizing is carried out. A variety of well-known compounds may be added in the washing step and the stabilizing step to prevent precipitation and to conserve water. For example, inorganic phosphoric acid, amino polycarbonate, organic amino polyphosphonate, organic phosphoric acid and other water softeners may be used to prevent precipitation; a bactericide and antibacterial agent may be used to prevent bacteria, scum and mildew; metal salts such as magnesium salt, aluminum salt and bismuth salts or surface active agents and a variety of hardening agents and the like may be used as needed to prevent a dry load and surface unevenness. Another possibility is to add the compound described in L.E. West, "Photographic Science and Engineering", vol. 6, 344 to 359, 1965. Adding a chelating agent and a bactericide is particularly useful.

The color photographic printing paper in the present invention may contain a variety of 1-phenyl-3-pyrazolidones to promote color developing. Typical examples of these are described in the

Specification of Japanese Laid-Open Patent 56-64339, the  
Specification of Japanese Laid-Open Patent 57-144547, the  
Specification of Japanese Laid-Open Patent 57-211147, the  
Specification of Japanese Laid-Open Patent 58-50532, the  
Specification of Japanese Laid-Open Patent 58-50536, the  
Specification of Japanese Laid-Open Patent 58-50533, the  
Specification of Japanese Laid-Open Patent 58-50533, the  
Specification of Japanese Laid-Open Patent 58-50534, the  
Specification of Japanese Laid-Open Patent 58-50535 and the  
Specification of Japanese Laid-Open Patent 58-115438 and the like.

Each of the abovementioned processes was carried out at 10°C to 50°C. Although a temperature of 33°C to 38°C is standard, the process can be promoted at higher temperatures and the processing time can be shortened. Conversely, the processing can be carried out at lower temperatures, the image quality can be improved and the stability of the processing solution can be improved. In addition, a process which involves using cobalt intensification or hydrogen peroxide intensification as described in West German Patent 2,226,770 or in United States Patent 3,674,499 can be used to conserve silver in the photosensitive material.

In addition, in continuous processing, a constant finish can be obtained by preventing fluctuations in the liquid composition by using a replenishing solution for the various processing solutions. The amount of replenishing solution used can be reduced to one-half


or to less than one-half of the standard replenishing amount to cut costs.

As indicated above, a sensitive material manufacturing technique and a developing processing system for it can be applied to color photographic printing paper in the regular negative/positive system, inverse color photographic printing paper, direct positive type color photographic printing paper or color photographic printing paper for use in color hard copy using output using a color scanner for the color photographic printing paper used in the seal print in the present invention.

#### **Practical Example-1**

We coated a photosensitive layer comprised of layers 1 through 7 on a polyethylene paper carrier which was approximately 120  $\mu\text{m}$  thick by laminating both sides and we produced a color photographic printing paper. The polyethylene on the side which had been coated with the first layer contained titanium dioxide and a tiny amount of ultramarine.

#### **(Composition of Photosensitive Layer)**

The numbers corresponding to each constituent indicate the amount coated on represented in units of g/ and indicated the silver conversion coating amount for the halogenated silver.

#### **First Layer (blue-sensitive layer)**

Salt bromide silver emulsion (bromide silver 80 mol %)	
	silver ..0.30
Yellow coupler (*1)	...0.70

Solvent for same (TNP)	...0.15
Gelatin	...1.20

**Second Layer (intermediate layer)**

Gelatin	....0.90
di-t-octyl hydroquinone	....0.05
Solvent for same (DBP)	....0.10

**Third Layer (green-sensitive layer)**

Salt bromide silver emulsifier (bromide agent 70 mol %)	silver 0.45
Magenta coupler (*2)	....0.35
Solvent for same (TOP)	....0.44
Color fading prevention agent (*3 / * 4)	....0.05 /0.10
Gelatin	....1.00

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**Fourth Layer (ultraviolet ray absorptive intermediate layer)**

ultraviolet ray absorption agent (*5/*6/*7)	...0.06/0.25/0.25
Solvent for same (TNP)	....0.20
Gelatin	...1.50

**Fifth Layer (red-sensitive layer)**

Salt bromide silver emulsion (bromide silver 50 mol %)	silver 0.20
Cyan coupler (*8/*9)	....0.2/0.2
Coupler solvent (TNP/DBP)	...0.10/0.20
Gelatin	0.9

**Sixth Layer (ultraviolet ray absorptive intermediate layer)**

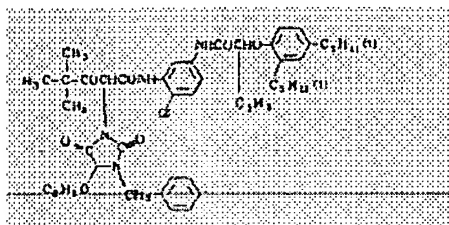
Ultraviolet absorption agent (*5/*6/*7)	...0.06/0.25/0.25
Solvent for same (DBP)	..0.20
Gelatin	..1.5

**Seventh Layer (protective layer)**

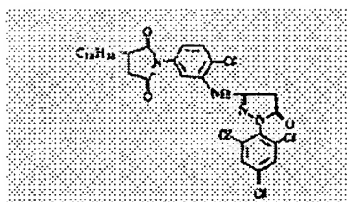
Gelatin	...1.5
---------	--------

Here, DBP is dibutyl phthalate; TOP is tri (n-octyl phosphate);  
and TNP is tri (n-nonyl phosphate).

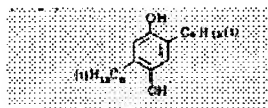
(\*1)



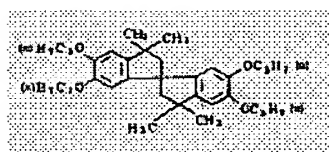
(\*2)



(\*3)

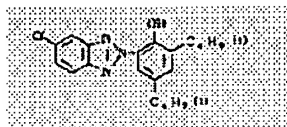


(\*4)

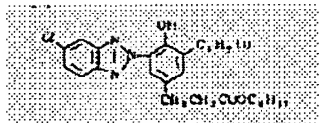




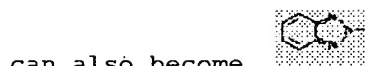
(\*5)



(\*6)



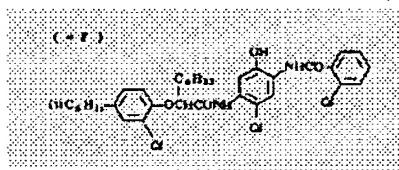
(\*7)



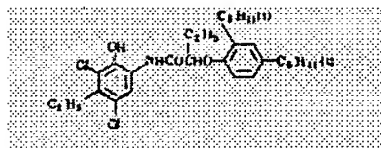
since the skeletal nucleus is a resonant structure

(\*8)

/350



(\*9)



We used the following pigments as the spectral sensitizing agent for each of the emulsion layers.

**Blue-sensitive emulsion layer:**

4- {5-chlor-2-[5-chloro-3-(4-sulfonate butyl) benzothiazoline-2-iridium methyl]-3-benzothiazolio } butane sulfonate triethyl ammonium salt ( $2 \times 10^{-4}$  mol per single halogenated silver mol).

**Green-sensitive emulsion layer:**

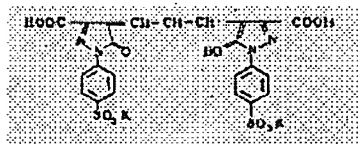
3,3'-di-( $\gamma$ -sulfopropyl)-5,5'-diphenyl-9-ethyl oxacarbocyanine sodium salt ( $2.5 \times 10^{-4}$  mol per single halogenated silver /mol).

**Red-sensitive emulsion layer:**

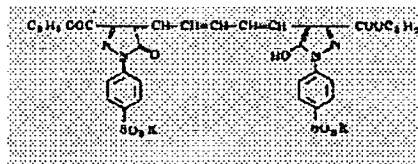
3,3'-di-( $\gamma$ -sulfopropyl)-9-methyl-thiadicarbocyanine sodium salt ( $2.5 \times 10^{-4}$  per single halogenated silver mol).

We used the following dyestuffs as an irradiation prevention dyestuff for each of the emulsion layers.

**Green-sensitive emulsion layer:**



**Red-sensitive emulsion layer:**



We labeled the photosensitive material "Sample 101".

Next, we produced Sample 102 and Sample A in the same way as we did above except that we made the changes indicated in Table 1 as follows. We provided gradation exposure using sensitometry using a

red · green and blue band pass filter having the spectral transmittance indicated in Figure 4 using an enlarger (Fujicolor Head 609, from Fuji Photo Film Ltd.) for these samples. Then, we carried out developing using the following processing steps.

<u>Processing Step</u>	<u>Temperature</u>	<u>Time</u>
Developing solution	33°C	3 min/30 sec.
Bleaching/fixing solution	33°C	1 min/30 sec.
Washing	28 to 35°C	3.0 min

#### Developing Solution

Nitrotriacetate · 3 Na	2.0 g
Benzyl alcohol	15 ml
Diethylene glycol	10 ml
Na <sub>2</sub> SO <sub>3</sub>	2.0 g
KBr	0.5 g
Hydroxyl amine sulfate	3.0 g
4-amino-3-methyl-N-ethyl-N-ethyl-N-[β-(methane sulfone amide) ethyl] -p-phenylene diamine · sulfate	5.0 g
Na <sub>2</sub> CO <sub>3</sub> (1 water salt)	30 g

We added water to make it 1 liter (pH 10.1)

#### Bleaching and Fixing Solution

Ammonium thiosulfate (54 wt %)	150 ml
Na <sub>2</sub> SO <sub>3</sub>	15 g
NH <sub>4</sub> [Fe (EDTA)]	55 g
EDTA · 2Na	4 g

We added water to make it 1 liter (pH 6.9)

We obtained the following coloring pigments. In addition, the spectral reflected concentration curve of the colored image obtained by three-color decomposition exposure is indicated in Figures 1 /351

through 3. The yellow coloring pigment is the pigment indicated in (1) -3 above; the magenta coloring pigment is the pigment indicated in (2) -1 above; and the cyan coloring pigment is a mixture of the pigments indicated in (4) - 2 above and the pigment indicated in pigment in (5) -1.

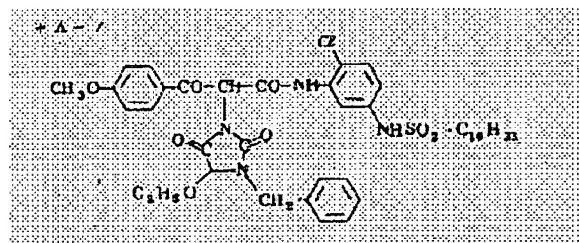
On the other hand, we printed on the abovementioned color photographic printing paper from the 35 mm color negative film and obtained photographs of people and scenery measuring approximately 148 mm (vertical dimensions) by approximately 100 mm (horizontal dimensions). We provided adhesive paper on the back surface and obtained a seal print. We used the adhesive paper described in Specification of Japanese Laid-Open Patent 61-179559. We peeled the photographic printing paper from the seal print, attached it to an official government-issued postcard and obtained a "photographic print with attached postcard".

The mount for this photographic print was the official postcard. The background of the mount shows through and the whiteness of the background of the original color print declines. As a result, there was little dissonance between the color on the background of the official postcard and the whiteness of the background of the color print. However, Sample 101 in the present invention had pigment with a higher chromaticness obtained than with A. As a result, the image in the print was beautiful with a luxurious feeling and it had a pleasant appearance.

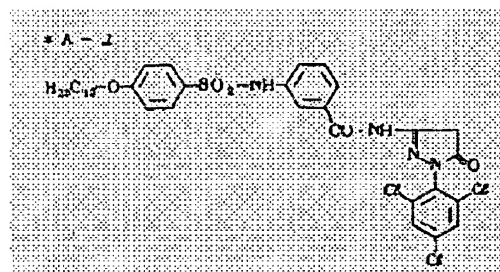
**Table 1**

Layer	Sample-101	Sample-102	Sample A
First layer	Yellow coupler *1	Coupler formed for (1)-4 *10	* A-1
Third layer	Magenta coupler *2	Coupler formed for (2)- 7 *11	* A-2
Fifth layer	Cyan coupler *8/*9	Coupler formed for *8/(5)-5 *12	* A-3

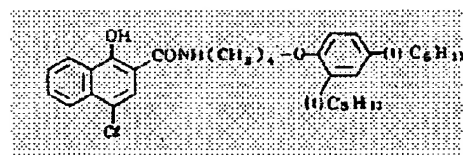
\*A -1

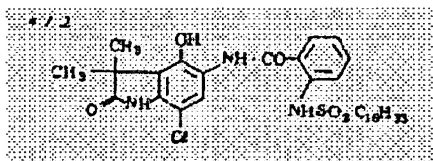
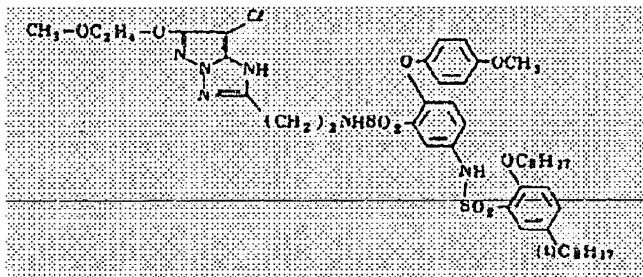
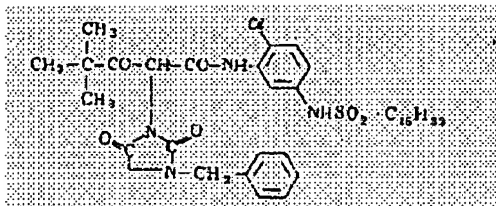


\*A -2



\*A -3





The spectral reflected concentration curve of the color print obtained by three-color decomposition exposure for Sample 101 and Sample A is indicated in Figure 1 through Figure 3. It was found that the photographic print obtained from Sample A had poor color separation and the image was muddy.

#### Practical Example-2

We substituted the same amount of coupler based on Practical Example-1 to form the pigment in the present invention, as indicated

in Table 2. We also added a non-water-soluble, organic solvent-soluble polymer in the present invention, added a compound belonging to general formula (12) or (13) and obtained Samples 103 through Sample 108. We provided gradation exposure using a three-color color decomposition filter based on that used in Practical Example-1 and carried out developing. We carried out high-humidity, heat durability test on each of the developed samples obtained. We set each of the developed samples aside for 12 days in a dark place at 80°C at 70 % RH and found the persistence rate of the pigments. The persistence rate of the pigments is indicated in Table 2 at a ratio (%) of the concentration following the test on the initial concentration of 1.5.

Based on the results, it can be seen that the "photographic print with attached postcard" obtained from the seal print can prevent the attractiveness of the image from deteriorating due to fading even under rigorous conditions. What should particularly be pointed out is that the degree of durability for the yellow pigment, magenta pigment and cyan pigment in the present invention can be balanced.

#### **Practical Example-3**

We roughened the surface of a polyethylene paper carrier approximately 80  $\mu$  thick laminated on both sides. We extruded low-density polyethylene and coated metal aluminum foil measuring approximately 10  $\mu$ m having a second type of diffusion reflectivity and laminated it and obtained a new carrier. We mixed an epoxy group

adhesive and an ionomer resin (both from Dupont Inc.) on the surface of the metal aluminum surface which had been laminated and disposed an undercoating approximately which was 0.2  $\mu\text{m}$  thick. We carried out corona discharge processing and disposed an undercoating approximately 0.1  $\mu\text{m}$  thick using gelatin and a hardening agent 2,4-dichlor-6-hydroxy-1,3,5-triazine. We obtained color photographic printing paper: Sample 109 and Sample 110 using a raw material indicated as Samples 109 and 110 in Practical /353 Example 1 and Table 2 on top of this.

We provided gradation exposure for Sample A, Sample 101, Sample 109 and Sample 110 passing through the three color decomposition filter and then carried out developing processing as follows.

- |                         |              |                       |
|-------------------------|--------------|-----------------------|
| 1. Color developing     | 35°C         | 45 seconds            |
| 2. Bleaching and fixing | 35°C         | 1 minute, 0 seconds   |
| 3. Washing              | 25°C to 30°C | 2 minutes, 30 seconds |

[Table 2] [see end of document]

The composition of the processing solution is as follows. /354

**Coloring and Developing Solution**

Water	800 cc
Diethylene triamine pentaacetate	1.0 g
Sodium sulfite	0.2 g
N,N-diethyl hydroxyl amine	4.2 g
Potassium bromide	0.01 g
Sodium chloride	1.5 g
Triethanol amine	8.0 g
Potassium carbonate	30 g
N-ethyl-N-( $\beta$ -methane sulfone	4.5 g



amide ethyl)-3-methyl-4- aminoaniline sulfate 4,4-  
diaminostyrene [as transliterated] group fluorescent  
whitener (Whitex 4 from Sumitomo Chemical Ltd.)

Added water	2.0 g
in KOH	1000 cc
	pH 10.25

#### Whitening and Fixing Solution

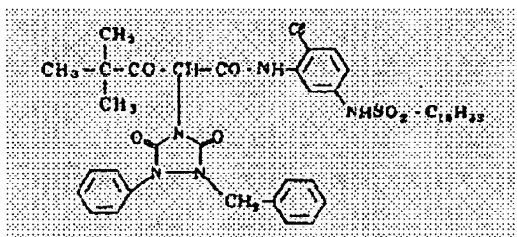
Ammonium thiosulfate (54 % by wt)	150 ml
Na <sub>2</sub> SO <sub>3</sub>	15 g
NH <sub>4</sub> [Fe (III) (EDTA)]	55 g
EDTA: 2 Na	4 g
Cooled acetic acid	8.61 g
Water added making total of	1000 ml
	(pH 5.4)

#### Rinsing solution

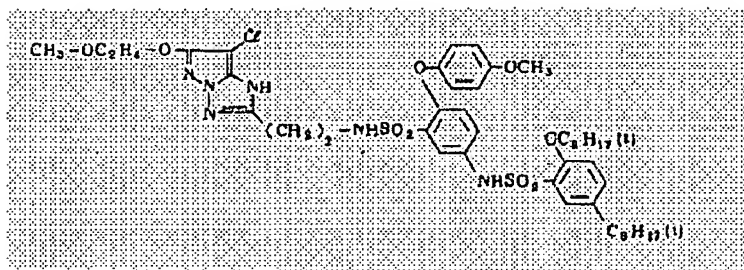
EDTA · 2 Na · 2 H <sub>2</sub> O	0.4 g
Water added making total of	1000 ml
	(pH 7.0)

Coupler used in Sample 110

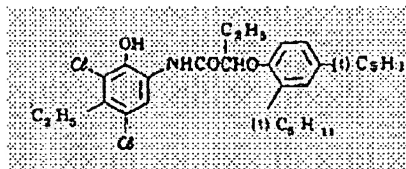
Coupler formed in pigment (1)-4



Coupler formed for pigment (2)-7



Coupler formed for pigment (4)-2



We carried out high humidity and heat durability tests based on Practical Example-1 and indicated the results in Table 2.

We indicated the spectral reflexive property of each of the colored images obtained for Sample 109 in Figure 1 through Figure 3 compared to Sample 101 and Sample A.

The photographic print from the seal print in the present invention has a high chromaticness and it can be seen that it has excellent durability relative to high humidity and heat.

### Practical Example -4

We produced the halogenated silver emulsion (7) for the blue-sensitive halogenated silver emulsion layer as follows.

(solution 8)

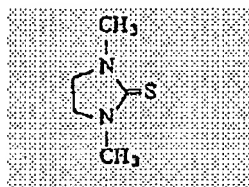
H <sub>2</sub> O	1000 cc
NaCl	5.8 g
Gelatin	25 g

(solution 9)

Sulfuric acid (1 N)	20 cc
---------------------	-------

(solution 10)

The following halogenated silver emulsion (1 %) 3 cc



(solution 11)

KBr	0.18 g
NaCl	8.51 g
Add H <sub>2</sub> O	130 cc

(solution 12)

AgNO <sub>3</sub>	25 g
add H <sub>2</sub> O	130 cc

(solution 13)

Pb (CH <sub>3</sub> COO) <sub>2</sub> (3 hydrogen/chlorine)	
(0.1 %)	28 cc

(solution 14)

KBr	0.70 g
NaCl	34.05 g
add H <sub>2</sub> O	285 cc

(solution 15)

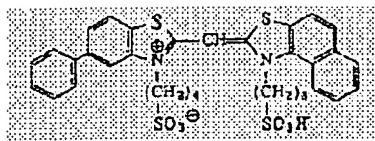
AgNO <sub>3</sub>	100 g
add H <sub>2</sub> O	285 cc

We heated (solution 8) to 60°C and added (solution 9) and (solution 10). Then, we added (solution 11) and (solution 12) simultaneously for 60 minutes. We added (solution 13) one minute after (solution 11) and (solution 12) were added. Five minutes after adding these, we lowered the temperature and desalted it. We added water and dispersed gelatin and adjusted it to pH 6.0. We obtained a single dispersion cubic salt silver bromide emulsion having an average grain size of 1.00  $\mu$ , a fluctuation coefficient of 0.11 and a silver bromide of 1 mol %. We added triethyl thiourea and silver chlorate to this emulsion and carried out optimal chemical sensitization. Then, we added  $5 \times 10^{-4}$  mol of the following spectral sensitizer (liter) per 1 mol of halogenated silver emulsion.

Comment [AS2]: Phrase/sentence missing

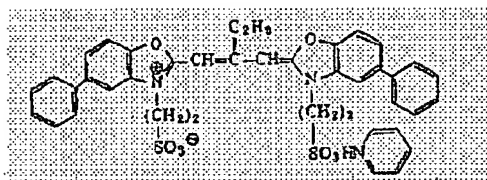
We prepared the halogenated silver emulsion (8) of the green-sensitive halogenated silver emulsion layer and the halogenated silver emulsion (9) of the red-sensitive halogenated silver emulsion by changing the amount of the chemicals in (solution 8) and (solution 10), the type and quantity of the spectral sensitizer and the temperature and time required for adding using the same method as indicated above. The spectral sensitizer (8) of the halogenated silver emulsion is the following (m) and the spectral sensitizer using the halogenated silver emulsion (9) is (n).

(1)

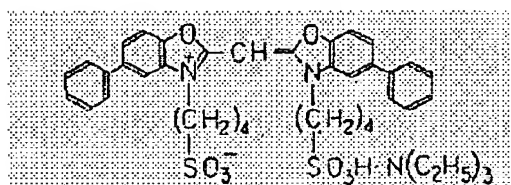


( $5 \times 10^{-4}$  mol added per 1 mol of halogenated silver)

(m)

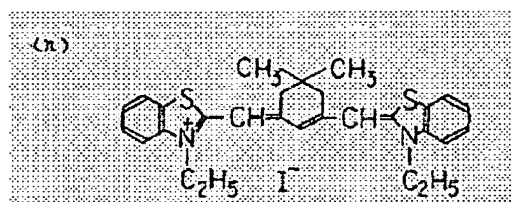


( $4 \times 10^{-4}$  mol added per 1 mol of halogenated silver)



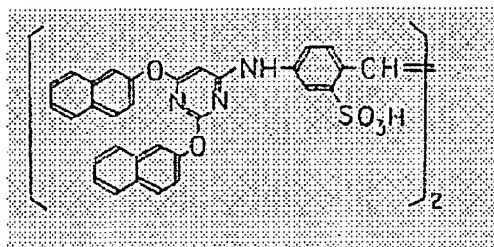
( $7.0 \times 10^{-5}$  mol per 1 mol of halogenated silver)

(n)



( $0.9 \times 10^{-4}$  mol per 1 mol of halogenated silver)

We added  $2.6 \times 10^{-3}$  mol of the following compound per 1 mol of halogenated silver for the red-sensitive emulsion layer.



We added 1-(5-methyl ureide phenyl)-5-mercaptopotetrazole at  $8.5 \times 10^{-5}$  mol,  $7.7 \times 10^{-4}$  mol and  $2.5 \times 10^{-4}$  per 1 mol of halogenated silver to the blue-sensitive emulsion layer, the green-sensitive emulsion layer and the red-sensitive emulsion layer.

The average grain size, fluctuation coefficient and halogen composition for halogenated silver emulsions (7) through (9) are indicated in Table 3.

We produced Sample 103 and Sample 104 by substituting the halogenated silver emulsion for the first layer, third layer and the fifth layer of Sample -101 and Sample -102 in Practical Example 1 with the abovementioned halogenated silver emulsions (7), (8) and (9) and provided the same type of gradation exposure as in Practical Example 1. Then we carried out the following processing and measured the sharpness and confirmed that the sharpness had been further enhanced.

Table 3

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Emulsion	Average Grain Size ( $\mu\text{m}$ )	Fluctuation coefficient (s/d)	Halogen composition	
			Br %	Cl %
(7)	1.00	0.09	1.0	99.0
(8)	0.44	0.10	0.4	99.6
(9)	0.53	0.09	1.0	99.0

(Processing Step)	(Temperature)	(Time)
Coloring and developing (preparation B)	35°C	45 seconds
Bleaching and fixing (preparation B)	35°C	45 seconds
Rinsing	28°C to 35°C	1 minute, 30 seconds

**(Coloring and Developing Solution Preparation B)**

Water	800 cc
diethylene triamine pentaacetic acid 5 Na salt	1.0 g
Sodium sulfite	0.2 g
N,N-diethyl hydroxyl amine	4.2 g
Potassium bromide	0.01 g
Sodium chloride	1.5 g
Triethanol amine	8.0 g
N-ethyl-N-( $\beta$ -methane) sulfone amide ethyl)	
-3-methyl-4-aminoaniline · sulfite	4.5 g
Potassium carbonate	30.0 g
4,4'-diaminostyrene [as transliterated] group fluorescent whitener (Whitex, from Sumitomo Chemical Ltd.)	2.0 g
Water added making overall quantity of	1000 cc (pH 10.1)

**(Bleaching and Fixing Solution Preparation-B)**

Water	700 cc
Ammonium thiosulfate (54 % by weight)	150 cc
Sodium sulfite	15 g
NH <sub>4</sub> [Fe. (III) (EDTA)]	55 g
EDTA · 2 Na (2 water/salt)	4 g
Cooled acetic acid	8.61 g
Water added making overall quantity of	1000 cc (pH 5.4)

(Rinsing solution preparation)

EDTA · 2 Na (2 water/salt)	0.4 g
Water added making a total of	1000 cc
	(pH 7.0)

4. Brief Explanation of Figures

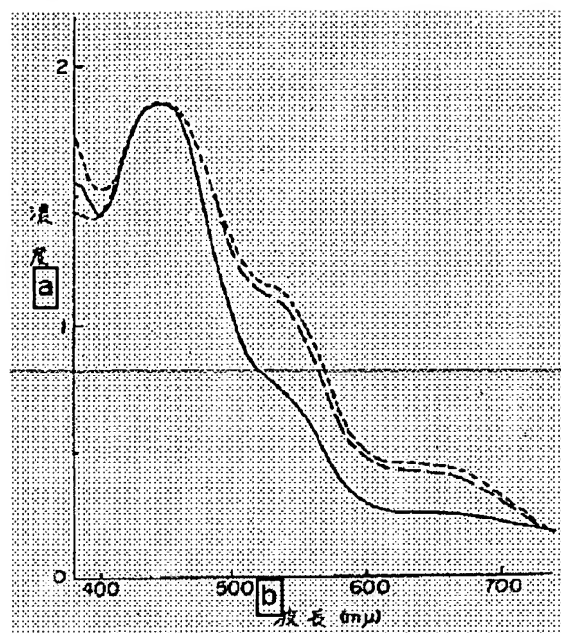
/355

Figure 1 is a spectral reflective concentration curve for Sample A, Sample 101 and Sample 109. Figure 2 is a spectral reflective concentration curve for the same type of magenta colored image. Figure 3 is a spectral reflective concentration curve for the same type of cyan colored image. Figure 4 is a spectral reflectance curve of the three-color decomposition filter. Where

\_\_\_\_\_ Sample 109  
- - - - - Sample 101  
- - - - - Sample A



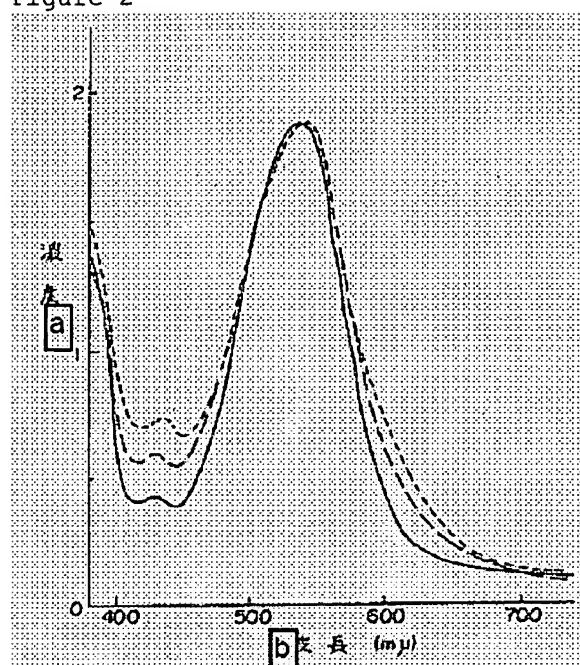
Figure 1



Key:

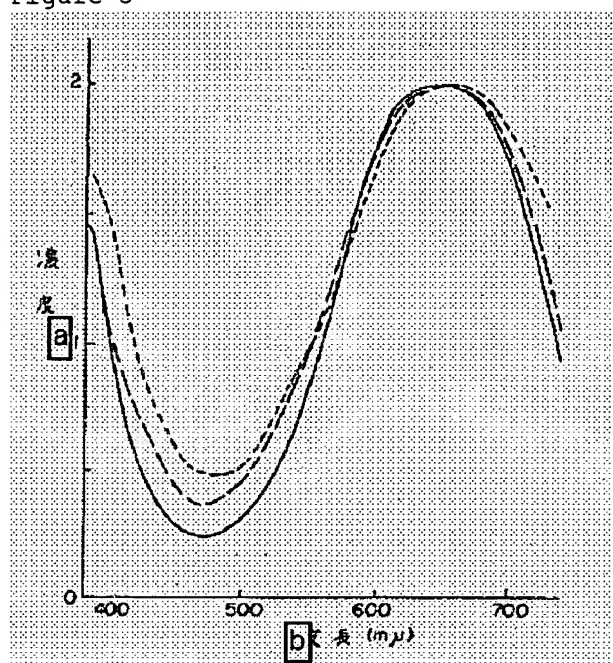
a) Concentration; b) wavelength (nm)

Figure 2



Key: a) concentration; b) wavelength (mμ)

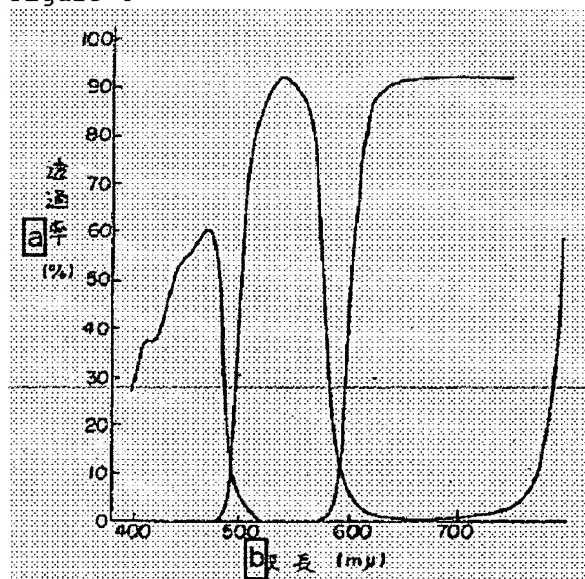
Figure 3



Key: a) concentration; b) wavelength (mμ)

Figure 4

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Key: a) concentration; b) wavelength (mμ)

Table 2 (page 353)

	First Layer (yellow coloring layer)			Third Layer (magenta coloring layer)			Fifth Layer (cyan coloring layer)			Durability (pigment persistence rate %)		
	Pigment (coupler coloring pigment)	Solvent Dispersed polymer	Anti-fading agent	Pigment (coupler coloring pigment)	Solvent Dispersed polymer	Anti-fading agent	Pigment (coupler coloring pigment)	Solvent Dispersed polymer	Anti-fading agent	Yellow	Magenta	Cyan
A	Y-1	TNP 0.15		M-1	TOP	*3 /*4	C-1	TNP/DBP		92	82	65
101	(1)-3	1		(2)-1	1	1		1		95	95	79
102	(1)-4	1		(2)-7	1	1		1		96	98	83
103	1	1		(2)-11	1	1		1		96	95	82
104	1	1		(2)-1	1	1				93	94	92
105	1	1		(2)-7	1	1				94	98	93
106	(1)-1	TNP 0.10 P-1 0.2		(2)-11	TOP 0.20 P-3 0.20	1		1		94	96	93
107	1	1		(2)-8	1			1		93	96	95
108	(1)-4	1		1	1			1		97	97	98
109	(1)-3	TNP 0.15	02.11	(2)-1	TOP	*3/*4				96	96	81
110	(1)-4	TNP 0.10 P-1 0.2	0.1	(2)-7	TOP 0.2 P-3 0.2	02-12 0.25				97	98	98

The amount of solvent, polymers and anti-fading agent are expressed in all cases in terms of g/m<sup>2</sup>  
1 indicates "improvement".